

# A More Sustainable and Cheaper One-Pot Route for the Synthesis of Hydrophobic Ionic Liquids for Electrolyte Applications

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An innovative one-pot synthetic process that uses water as the only processing solvent was used to obtain ionic liquids (ILs) in a yield of approximately 95 mol% and purity greater than 99.3 wt% (< 2 ppm each of lithium, bromide and moisture) in a processing time of 1 h. Since no heating is needed for carrying out the reaction and no purification through sorbents is required, energy, time and chemicals can be saved to minimize waste production. The physicochemical and electrochemical

validation, including tests in batteries, reported herein shows that the above-mentioned ILs have properties analogous to those of ILs prepared by standard reported procedures and show high performance without any further purification step through sorbents. These characteristics, in combination with low cost, easy execution and scale-up, sustainability and versatility, make the one-pot process even more appealing, especially for industrial-scale applications.

## Introduction

Ionic liquids (ILs) are a particular class of fluids with unique physicochemical peculiarities,<sup>[1,2]</sup> which are opening uses in a wider and wider variety of applications,<sup>[3–10]</sup> including electrochemical devices.<sup>[11–13]</sup> ILs are considered to be innovative and more selective replacements for organic solvents. In electrochemical systems, ILs have been proposed to replace hazardous alkyl carbonates<sup>[14,15]</sup> to improve the safety of final devices.

However, ILs are still niche products without wide application, as they are rather expensive. In the near future, large-scale industrial production is expected to remarkably reduce their final costs, which mainly depend on those of the chemicals and the synthesis/purification process. Hydrophobic ILs based on imidazolium, pyrrolidinium, piperidinium or tetraalkylammonium cations and bis(perfluoroalkylsulfonyl)-imide anions have been found to be among the most viable IL materials for electrochemical systems.<sup>[13]</sup> Their anions are prepared from expensive reagents such as alkali metal bis(perfluoroalkylsulfonyl)imide salts, which are obtained by fluorine chemistry, whereas the cations are synthesized from rather

cheap chemicals such as alkyl imidazoles, alkyl pyrrolidines, alkyl piperidines, trialkyl amines and alkyl halides (especially chlorides and bromides). The cost of the synthesis route is also related to the processing conditions (i.e., steps, time, temperature, required energy, solvent type, need of purifier materials, waste production, etc.).


Previously, we have designed a cheaper procedure for synthesizing hydrophobic ILs with lower environmental impact that requires only water as the processing solvent.<sup>[16]</sup> Organic solvents (e.g., dichloromethane, acetonitrile, acetone), which are commonly used in the synthesis of ILs<sup>[17]</sup> and are generally not desired in the chemical industry, since they need full recycling, which further increases the overall cost of the IL, to avoid their emission into the environment. Also, a suitable recycling route was designed to minimize the waste amount.<sup>[16]</sup> Hydrophobic ILs are synthesized by a two-step process: 1) preparation of a precursor; 2) metathesis reaction of the precursor with an alkali metal salt to obtain the desired IL.

In this work we further developed the aqueous route to design a cheaper, faster, one-pot synthetic process, which allows ILs, mainly hydrophobic but also hydrophilic ones, to be obtained in a one-hour single-step process. In addition, the one-pot process is thermally self-sustainable, that is, no heating is required for carrying out the reaction, with remarkable savings of processing energy and time. Water is used as the only processing solvent. The study was performed on *N*-methyl-*N*-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide (PYR<sub>13</sub>TFSI) as a reference IL. However, the one-pot route is applicable to the synthesis of various IL families. The quality of the obtained IL was validated, and the influence of the processing conditions was investigated. The possibility of further purification through sorbents was also verified, and its effect on the physicochemical/electrochemical properties was studied.

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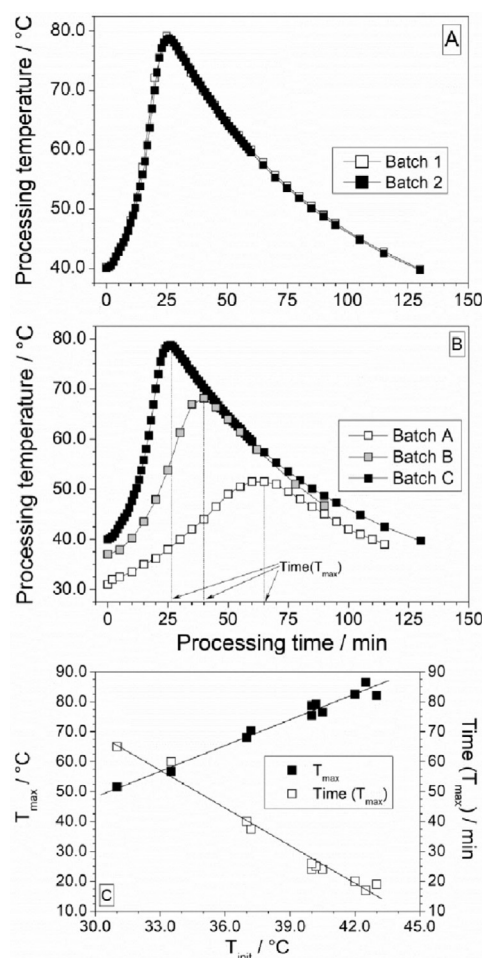
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## Results and Discussion

The synthesis of ILs generally requires a processing temperature ranging from 50 to 80 °C<sup>[16,18]</sup> to promote the alkylation of amines, for example, saturated cyclic (pyrrolidine, piperidine), linear (NR<sub>3</sub>) or heteroaromatic (imidazole, pyridine), with alkyl halide.<sup>[16,18]</sup> However, the one-pot route does not require any heating, as the processing temperature is provided by the heat resulting from the exothermal dissolution of *N*-methylpyrrolidine (mainly) and LiTFSI in water, and also by the alkylation reaction itself. Therefore, once initiated, the process continues spontaneously until formation of the IL; for example, the alkylation of *N*-methylpyrrolidine with 1-bromopropane gives the PYR<sub>13</sub>Br precursor, which quickly reacts with LiTFSI<sup>[16,19]</sup> to give PYR<sub>13</sub>TFSI. The one-pot process can be easily scaled up and extended to a wide variety of hydrophobic ILs without any substantial modification of the procedure, and this makes it of interest with a view to industrial applications.

The progress of the one-pot process is indicated by the evolution of the processing temperature (Figure 1), which shows a bell shape with relatively fast increase. This clearly suggests that 1) the overall process is self-sustaining, as the temperature increases without any external heating; 2) the chemical reactions are initially much faster, as indicated by the rise of the processing temperature, and this suggests that the IL is mostly obtained during this time period; 3) once the IL is mainly formed, the process proceeds much more slowly to completion, as indicated by the progressive temperature decay. The excellent reproducibility of the time evolution of the processing temperature (Figure 1A) is noteworthy, that is, overlapping profiles are obtained for two analogous batches subjected to identical operating conditions, which indicate that the one-pot process does not occur randomly. Conversely, different time-temperature profiles are observed for different initial processing temperatures (Figure 1B). For instance, an increase in  $T_{\text{init}}$  leads to a higher processing temperature and faster temperature rise. This is better evidenced in Figure 1C, which shows the dependence of the maximum temperature  $T_{\text{max}}$  reached during the one-pot reaction (Figure 1B) and of the corresponding time  $t(T_{\text{max}})$  (Figure 1B) as a function of  $T_{\text{init}}$ , which ranged from 30 to 45 °C. The  $T_{\text{max}}$  value linearly increases with increasing  $T_{\text{init}}$  value, whereas  $t(T_{\text{max}})$  linearly decays with increasing  $T_{\text{init}}$ . Therefore, the one-pot process may be governed by the initial temperature.

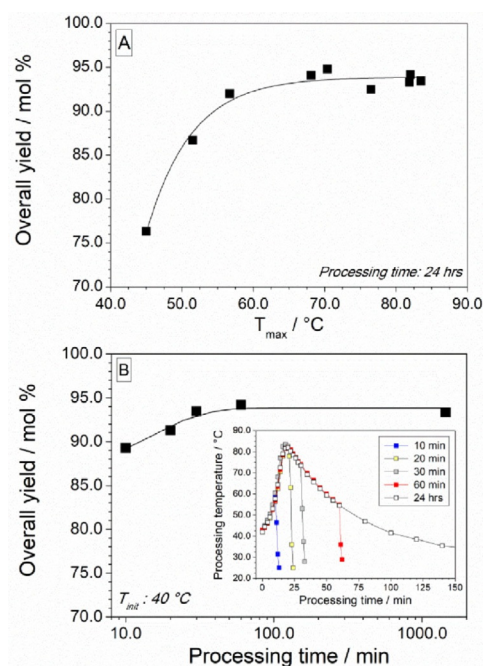
The efficiency of the one-pot route was investigated in dependence on the operating conditions. The overall yield of the process increases from 76 to 95 mol% when  $T_{\text{max}}$  is raised from 45 to 70 °C (Figure 2A). The processing time was fixed at 24 h to allow completion of the chemical reactions. Further increase of  $T_{\text{max}}$  above 70 °C does not lead to any gain in yield. We note that the maximum yield does not exceed 95% (referred to the IL phase, which was weighted upon rinsing and vacuum drying), because the remaining fraction ( $\approx 5\%$ ) dissolves in the aqueous phase during the one-pot process.<sup>[16,20]</sup> For instance, even if the IL is insoluble in water, its TFSI anions are bound to the Li<sup>+</sup> cations,<sup>[21,22]</sup> which are strongly coordinated by the water molecules. This Li<sup>+</sup>...TFSI...H<sub>2</sub>O triple coordination is the



**Figure 1.** Evolution of processing temperature versus processing time for different PYR<sub>13</sub>TFSI batches starting from the same (A) or different (B) initial temperatures. C) Dependence of the maximum temperature  $T_{\text{max}}$  reached during the one-pot process and of the corresponding time at  $T_{\text{max}}$  as a function of the initial processing temperature  $T_{\text{init}}$ .

driving force that causes partial dissolution of the IL. However, previous work<sup>[16]</sup> has shown how this IL fraction can be fully recovered.

Figure 2B plots the process yield as a function of the processing time. For instance, analogous PYR<sub>13</sub>TFSI batches, starting from the same initial temperature (40 °C), were prepared and, upon different processing times (from 10 to 60 min), quickly cooled to room temperature in a water/ice bath. A further batch was processed for 24 h for comparison. The time evolution of the processing temperature for different PYR<sub>13</sub>TFSI batches is shown in the inset of Figure 2B. The yield increases on going from a processing time of 10 to 60 min. No additional gain in yield is observed for further increases of the processing time. The completion of the one-pot process after 1 h is also confirmed by the very low residual Br content ( $< 2$  ppm) detected in the IL. Conversely, much higher overall Br contents (ca. 600 and 400 ppm) were recorded for shorter processing times (30 and 45 min; see the Supporting Information, Figure S1), ascribable to unconverted 1-bromopropane, which is insoluble in water and cannot be removed through the rinsing



**Figure 2.** Dependence of the overall yield of the one-pot process as a function of  $T_{\max}$  (A, 24 h processing time) and of the processing time (B,  $T_{\text{init}} = 40^\circ\text{C}$ ). The inset in B) shows the evolution with time of the processing temperature for different  $\text{PYR}_{13}\text{TFSI}$  batches.

steps. This suggests that the alkylation process of *N*-methylpyrrolidine was not driven to completion.

To summarize, the one-pot route can be easily driven to completion in aqueous medium by simply tuning the initial temperature of the process, that is, by varying the amount of the water solvent. For an initial temperature of  $40^\circ\text{C}$ , which corresponds to a  $T_{\max}$  value of  $80^\circ\text{C}$ , the process yield reaches the maximum possible value (95 mol%) in a processing time of 1 h. These features are of particular relevance with a view to industrial applications, by making the route highly sustainable and allowing remarkable savings in processing time and energy.

$^1\text{H}$  NMR spectroscopy verified that  $\text{PYR}_{13}\text{TFSI}$  was indeed synthesized, as indicated by the assignment in Figure S2. No difference was observed on comparing the NMR spectrum of  $\text{PYR}_{13}\text{TFSI}$  obtained by the one-pot process with that of the same IL material prepared by the conventional two-step route.<sup>[16,19]</sup> The presence of deuterated DMSO and  $\text{H}_2\text{O}$  is evidenced by reproducible features that appear in both NMR spectra.

The one-pot process allows clear and anhydrous ILs to be obtained with lithium and bromide contents below 2 ppm. Five consecutive rinsing steps are required for fully removing the LiBr side product from the IL, in confirmation of the previously reported results.<sup>[16,19]</sup> The moisture content was always lower than 2 ppm. Halide and/or water are very undesirable impurities for ILs used in electrochemical devices. For instance, halides can be reduced to halogens, and water can result in parasitic oxidation or catalyze massive reduction of the IL

electrolyte<sup>[3,17]</sup> and thus narrow its electrochemical stability window.

The purity of the  $\text{PYR}_{13}\text{TFSI}$  IL prepared by the one-pot process exceeded 99.3 wt%. This value was determined by taking into account: 1) the stoichiometric amount and impurity content of all used chemicals ( $\text{PYR}_1$  98 wt%, 1-bromopropane 99 wt%,  $\text{LiTFSI} > 99.99$  wt%); 2) the feasibility of fully removing lithium and bromide. In addition, further water-soluble impurities can be removed in the rinsing steps (in water) of the IL.

The IL prepared through the one-pot route was subjected to physicochemical and electrochemical validation to verify its feasibility in practical devices. Also, the performance of the pristine IL was compared with that of an identical material subjected to further purification through activated carbon, which is currently used<sup>[16,17,19]</sup> for achieving high purities owing to its ability to retain impurities.

Preliminary UV/Vis measurements were performed to investigate the effect of different carbon (Aldrich, Darco-G60)/IL weight ratios. Before use, the sorbent material was cleaned in deionized water according to a procedure reported elsewhere.<sup>[18]</sup> Separate  $\text{PYR}_{13}\text{TFSI}$  batches (50 g each), prepared by the one-pot route, were treated with different amounts of the thus-cleaned activated carbon. The IL and carbon were loaded into a glass reactor and intimately mixed at ambient temperature for 3 h. The IL/carbon slurries were carefully vacuum-filtered by using an oil-free pump and Teflon filter membranes with porosity smaller than  $0.2\ \mu\text{m}$  to separate the purified IL, which was clear and colorless as opposed to the yellowish pristine IL, from the sorbent material. Finally, the IL was vacuum-dried according to the protocol described in the Experimental Section. UV/Vis measurements (Figure S3) showed a progressively strong reduction of the absorbance profile on going from a carbon/ $\text{PYR}_{13}\text{TFSI}$  weight ratio of 0.07:1 to 0.28:1. The area between the UV/Vis trace in the 260–600 nm range (Figure S3) and the x axis, which was determined by a fitting program, is directly proportional to the amount of impurities contained in the volume of IL sample subjected to the spectrophotometric measurements. As identical volumes of each IL sample were analyzed, a direct proportionality between the area and the impurity concentration can be reasonably assumed.<sup>[18]</sup> Therefore, taking into account the purity of the pristine sample (99.3%) and the different areas determined for each spectrophotometric curve, treatment with activated carbon at a weight ratio of 0.28:1 allows the IL purity to be enhanced to greater than 99.93%.

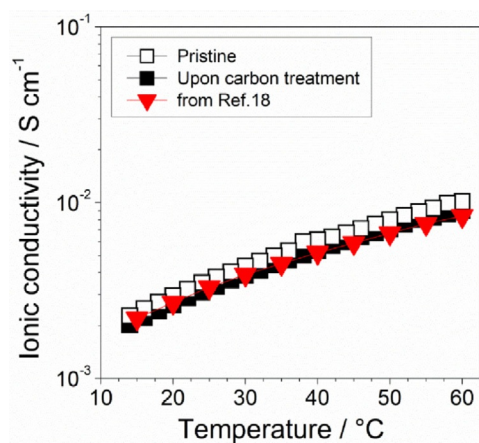
The IL samples for physicochemical and electrochemical validation were prepared by synthesizing a 100 g batch of  $\text{PYR}_{13}\text{TFSI}$  according to the one-pot route described in the Experimental Section, that is, the starting temperature was fixed at  $40^\circ\text{C}$  and the processing time was limited to 1 h. Subsequently, the batch was divided into two identical fractions: the first (pristine) was separately collected, whereas the second (purified) was processed with activated carbon in 0.28:1 weight ratio. Finally, both IL fractions were vacuum-dried by the above-described procedure and investigated.



Density measurements at 20 °C gave values in very good agreement with previously reported data.<sup>[19]</sup> No difference was observed between the pristine and processed ILs (Table 1). The ion-transport properties were validated, in terms of conductivity versus temperature dependence, for both pristine and purified samples. The results (Figure 3) show practically no differ-

**Table 1.** Densities and conductivities of PYR<sub>13</sub>TFSI as obtained from the one-pot process (pristine) and upon further purification with activated carbon. The data from Ref. [19] are reported for comparison purpose.

	From Ref. [19]	Pristine	Carbon-treated
Density <sup>[a]</sup> [g cm <sup>-3</sup> ]	1.432 ± 0.001	1.433 ± 0.001	1.434 ± 0.001
Ionic conductivity <sup>[a]</sup> [S cm <sup>-1</sup> ]	(2.7 ± 0.3) × 10 <sup>-3</sup>	(3.3 ± 0.4) × 10 <sup>-3</sup>	(2.6 ± 0.3) × 10 <sup>-3</sup>
[a] T = 20 °C.			



**Figure 3.** Conductivity versus temperature for PYR<sub>13</sub>TFSI as obtained from the one-pot process (pristine) and upon further processing with activated carbon. The data (taken from Ref. [18]) of an analogous sample (red triangles), prepared by a different synthetic route, are shown for comparison. The measurements were carried out by means of a heating temperature scan at a rate of 1 °C h<sup>-1</sup>. The error bars lie within the data markers.

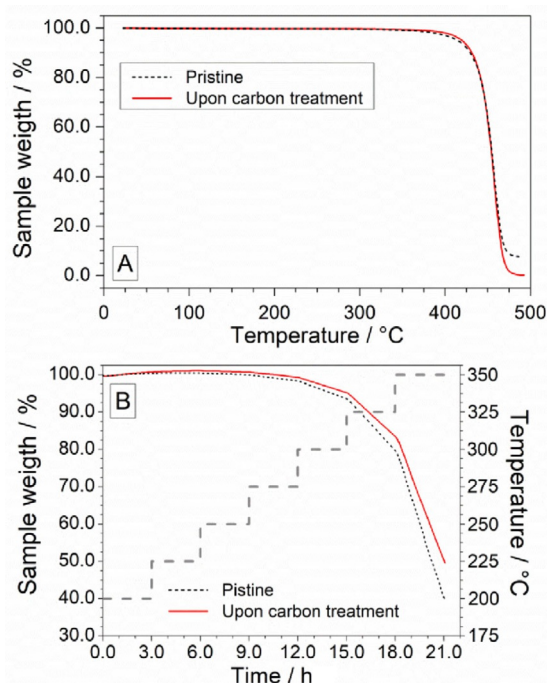
ence (error bar within the data markers) in ion conduction between pristine PYR<sub>13</sub>TFSI and the same IL processed with activated carbon, and also with respect to the analogous IL prepared by a different synthetic route<sup>[19]</sup> (Table 1).

Thermogravimetric analysis (TGA, Figure 4) revealed that thermal degradation occurs at the same temperature in both pristine and purified ILs, and both investigated one-pot ILs are thermally stable up to 250 °C, as evidenced by isothermal step measurements (Figure 4B). Above this temperature, decomposition processes (at a rate progressively increasing with increasing temperature) take place in both IL samples with a higher weight loss for the pristine IL, which is likely due to faster degradation kinetics ascribable to its lower purity.

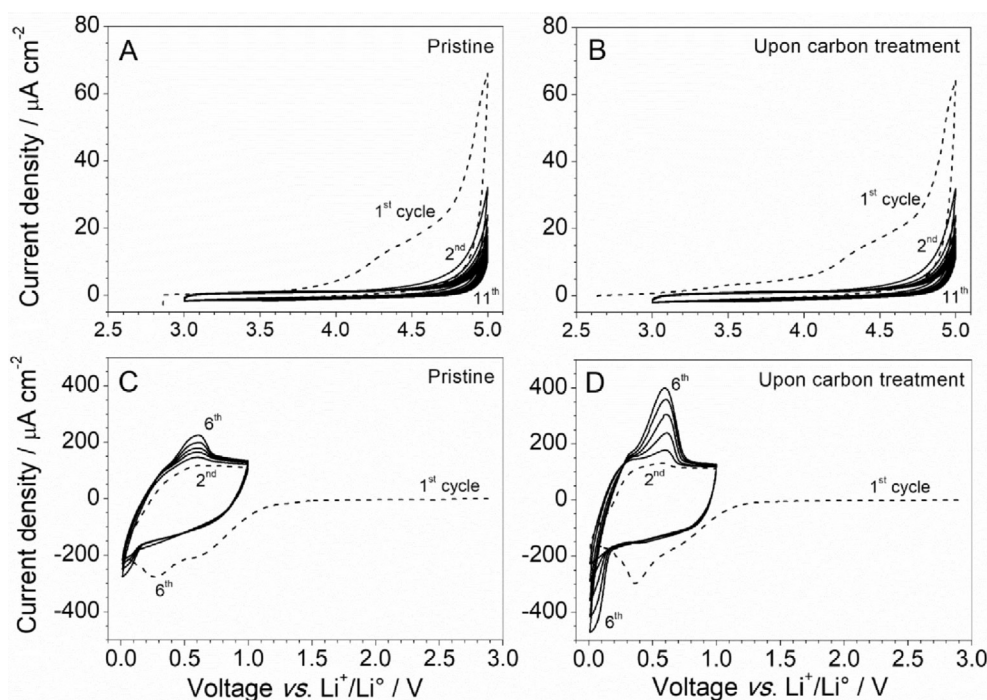
The electrochemical stability was validated by cyclic voltammetry (CV) with carbon working electrodes, as they allow much better simulation of the behavior of electrolytes in practical devices compared with inert electrodes.<sup>[23]</sup> Repeated

anodic CV scans (Figure 5A and B) evidence, in the first cycle, relevant reduction of the residual current density (i.e., < 5 μA cm<sup>-2</sup>) well above 4.5 V for the LiTFSI-PYR<sub>13</sub>TFSI electrolytes containing both pristine (Figure 5A) and purified (Figure 5B) one-pot IL. This behavior suggests irreversibility of the oxidation phenomena occurring during the first anodic scan and rapid consumption of impurities. No improvement of the anodic stability is observed in the IL processed with activated carbon (Figure 5B). In addition, no appreciable corrosion was detected, despite the TFSI anion being known to be slightly corrosive to aluminum substrate,<sup>[24,25]</sup> and this provides support for the low impurity content in both the one-pot ILs, since impurities and moisture can catalyze degradation phenomena, and likely for the protective role of the working-electrode carbon layer on the Al foil. Consecutive cathodic CV scans (Figure 5C and D) show the feasibility of reversibly intercalating Li<sup>+</sup> cations in IL electrolytes, even those directly prepared by the one-pot route without any further purification step through carbon (Figure 5C), with good efficiency and no appreciable electrolyte degradation. Growth of a stable solid electrolyte interphase<sup>[23]</sup> is seen even for the pristine IL (Figure 5C), as evidenced by a broad cathodic shoulder around 0.7 V (vs. Li<sup>+</sup>/Li).

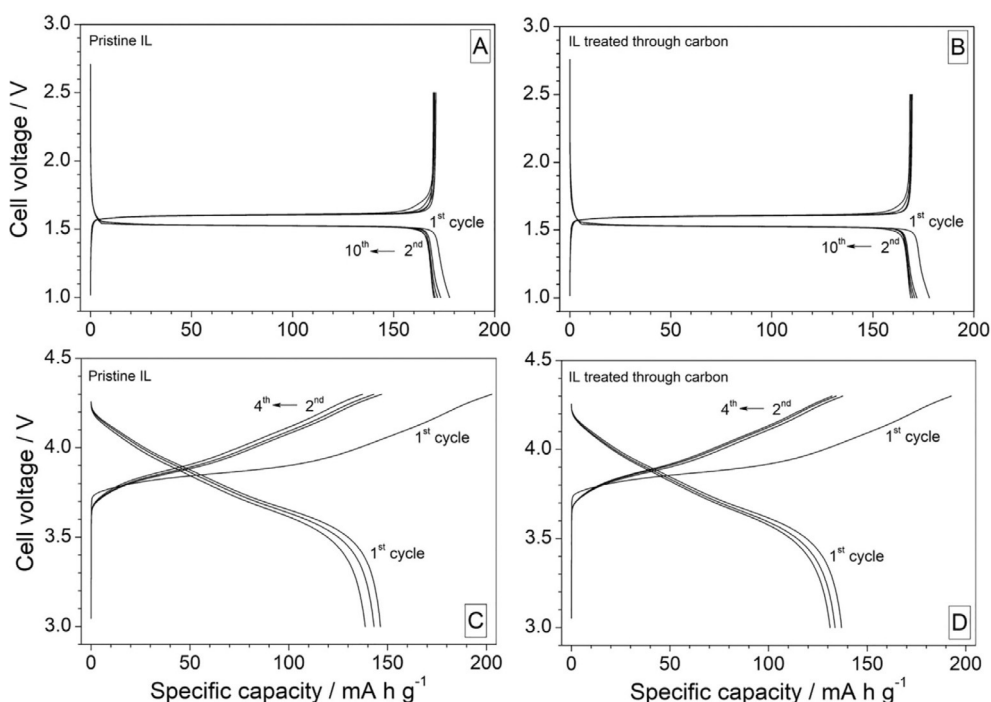
Preliminary tests in Li/lithium titanate oxide (LTO) (Figure 6A and B) and Li/lithium nickel manganese cobalt oxide (NMC) (Figure 6C and D) revealed high reversibility of the Li<sup>+</sup> intercalation process in the one-pot-IL electrolytes. The LTO and NMC



**Figure 4.** Variable-temperature (A, 10 °C min<sup>-1</sup> scan rate) and isothermal (B) TGA traces of PYR<sub>13</sub>TFSI as obtained from the one-pot route (pristine) and upon processing with activated carbon. The temperature/time profile (dotted grey trace) at which the isothermal measurements were run is shown in (B).



**Figure 5.** Anodic (A and B) and cathodic (C and D) CVs of LiTFSI/PYR<sub>13</sub>TFSI (1/9) electrolytes prepared with IL as obtained from the one-pot process (pristine, A and C) and upon processing with activated carbon (B and D). Carbon working and lithium counter electrodes were used. Scan rate: 1 mV s<sup>-1</sup>. Temperature: 20 °C.



**Figure 6.** Voltage versus capacity profiles of Li/LTO (A and B) and Li/NMC (C and D) half-cells. The LiTFSI/PYR<sub>13</sub>TFSI (1/9) electrolyte was prepared from PYR<sub>13</sub>TFSI as obtained from the one-pot process (pristine, A and C) and upon processing with activated carbon (B and D). Current rate: 0.1 C. Temperature: 20 °C.

electrodes exhibited reversible capacities of 170 and 140 mA h g<sup>-1</sup>, corresponding to about 100 and 64% of the theoretical values,<sup>[16,27]</sup> respectively, in both the pristine and puri-

fied ILs. For instance, no gain in terms of capacity and efficiency was observed if the IL was further purified with carbon. It is noteworthy that the pristine IL electrolyte (i.e., not subjected

to any treatment with sorbents), despite a purity that is not extremely high (99.3 %), can be successfully applied in electrochemical devices operating at up to 4 V.

To summarize, the electrochemical and physicochemical validation tests revealed how the characteristics of ILs obtained by a cheaper and more sustainable one-pot route that avoids additional purification steps with sorbents approach those of analogous materials prepared by conventional procedures. For instance, further treatment with activated carbon does not lead to any appreciable improvement of the transport, thermal and electrochemical properties of the IL, even though its purity is enhanced from 99.3 to 99.93 %.

This suggests that extremely high purities are not always needed, even for applications in electrochemical devices. Conversely, an additional sorbent-based purification step, if not strictly required, could make the one-pot process less appealing, because 1) an organic solvent should be used to both decrease the viscosity of the IL/carbon slurry and to recover the IL fraction trapped by the sorbent material,<sup>[19]</sup> which leads to a greater environmental impact of the overall process; 2) the sorbent materials and organic solvents should be recycled and recovered to minimize waste and to avoid emission of polluting vapors to the environment; 3) the increased processing energy/time and amount of chemicals, as well as the need for a bigger production plant, increase the final cost of the IL. Therefore, the one-pot process offers a cheaper, sustainable, faster, simpler and scalable method for synthesizing ILs with good physicochemical and electrochemical performance, which makes this route appealing with a view to large-scale industrial applications.

## Conclusion

An innovative single-step process using water as the only processing solvent, was designed to synthesize *N*-methyl-*N*-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide with a yield around 95 mol% and purity of 99.3 wt%. In particular, Li<sup>+</sup>, Br<sup>-</sup> and H<sub>2</sub>O contents were found to be lower than 2 ppm. This procedure can be extended to a large variety of hydrophobic ILs. Processing time no longer than 1 h was required without providing any energy for running the one-pot process. Even though additional treatment with activated carbon enhanced the purity to 99.93 wt%, no practical improvement in terms of physicochemical and electrochemical properties was observed, also with respect to those of analogous materials prepared through conventional processes. The resulting IL was tested as electrolyte component for Li-ion cells, in which it yielded good performance in spite of the high operating voltage (up to 4 V). These characteristics, in combination with the sustainability, lower cost, easier execution, versatility and scalability, make the one-pot route much more appealing, even for industrial applications, especially if extremely high purities are not required.

## Experimental Section

*N*-Methylpyrrolidine (PYR<sub>1</sub>, Sigma-Aldrich, ≥ 98 wt%), 1-bromopropane (Sigma-Aldrich, ≥ 99 wt%), lithium bis(trifluoromethylsul-

fonyl)imide (LiTFSI, 3 M, battery grade, > 99.99 wt%), were used as received. A Millipore ion-exchange resin deionizer provided deionized water (processing solvent).

A slight excess of PYR<sub>1</sub> (1 wt%) and LiTFSI (2 wt%) with respect to the stoichiometric amount of 1-bromopropane was used to increase the reaction yield.<sup>[16]</sup> The appropriate amounts of PYR<sub>1</sub> and LiTFSI were dissolved in deionized water in two different flasks. The PYR<sub>1</sub>/H<sub>2</sub>O and LiTFSI/H<sub>2</sub>O weight ratios, which were chosen to fully dissolve the chemicals without lowering the initial temperature of the solutions below 40 °C, were 2/3 and 5/1, respectively. The two solutions were quickly transferred to a glass reactor containing the appropriate amount of 1-bromopropane. To investigate the effect of temperature on the reaction, the temperature of the PYR<sub>1</sub>/H<sub>2</sub>O and LiTFSI/H<sub>2</sub>O solutions was adjusted prior to addition to 1-bromopropane in the glass reactor. Basically, *T*<sub>init</sub> is taken as the initial temperature of the overall solution. As detailed in Results and Discussion, this parameter plays a key role in the one-pot synthesis. Particular care was taken to minimize the heat release to the surroundings by using a thermally insulated reactor. No heating was needed for carrying out the one-pot reaction, the temperature of which was continuously checked as a function of the processing time by a thermometer in the glass reactor.

The chemicals and water were intimately mixed in the reactor, and after a selected reaction time the reactor was quickly cooled down to room temperature with an ice/water bath to allow phase separation. The (upper) aqueous phase containing the lithium bromide side product and excess LiTFSI, was separated from the water-insoluble IL by vacuum aspiration. Then, PYR<sub>13</sub>TFSI was rinsed with deionized water to remove residual LiBr and LiTFSI.<sup>[16,17]</sup> The water/PYR<sub>13</sub>TFSI volume ratio was fixed at 1/1 in the rinsing steps, which were repeated until disappearance of bromide in the aqueous phase (Br<sup>-</sup> detected by adding 0.1 N AgNO<sub>3</sub> to give an AgBr precipitate). Finally, the IL was vacuum-dried (with oil-free pumps) at 80 °C (rotary evaporator) for 2 h and then at 120 °C (glass oven) overnight. IL batches of 80–100 g were prepared for better investigating the effect of the processing conditions.

The chemical structure of PYR<sub>13</sub>TFSI was validated by <sup>1</sup>H NMR measurements with an Avance III Bruker (Billerica) spectrometer. The spectra were recorded with a BBFO broadband probe (Bruker) in deuterated DMSO (Sigma-Aldrich, > 99 wt%) as solvent. The peaks were assigned on the basis of the chemical shifts and integrals with DMSO signal as reference (NMR δ(<sup>1</sup>H) = 2.49 ppm).

The residual contents of Li<sup>+</sup>, Br<sup>-</sup> and H<sub>2</sub>O were determined by atomic absorption spectroscopy (SpectrAA mod. 220 Spectrometer), X-ray fluorescence spectrometry (Shimadzu energy-dispersive EDX-720 spectrometer, rhodium foil as X-ray source) and Karl Fisher titration (Mettler Toledo DL32, located in an argon-atmosphere glove box with water content < 10 ppm), respectively. The purity was checked by UV/Vis spectrophotometry (UV-1800 Shimadzu spectrophotometer) in the wavelength range from 190 to 700 nm (0.5 nm resolution). Polypropylene cuvettes with a 6 μm-thick circular (10 mm diameter) Mylar window and quartz cuvettes (10 mm optical path) were used for the X-ray fluorescence and UV/Vis measurements, respectively, which were performed on PYR<sub>13</sub>TFSI samples previously diluted (1:5 volume ratio) in ethanol (Carlo-Erba, > 99.5 wt%). Density measurements were performed at 20 °C by using a Mettler Toledo DE40 density meter located in a dry room (dew point below -65 °C).

TGA was performed with a PerkinElmer Pyris Diamond TGA/DTA calorimeter. The PYR<sub>13</sub>TFSI samples (ca. 5 mg) were housed in alumina pans and investigated in argon atmosphere. Variable-temper-



ature TGA was performed by running heating scans from room temperature to 500 °C (10 °C min<sup>-1</sup>), whereas isothermal TGA measurements, which allow better simulation of the (thermal) behavior in practical devices, were run at different temperature steps (3 h each).

The ionic conductivity was determined in the temperature range of 15–60 °C (Binder GmbH MK53 climatic chamber) by an AMEL 160 conductivity meter. The IL samples, which were manipulated in a dry room, were housed in sealed, glass conductivity cells (AMEL 192/K1) equipped with two porous platinum electrodes (cell constants around 1.00 ± 0.05 cm<sup>-1</sup> were verified by means of calibration solutions of known conductivity). The cells were subjected to an appropriate protocol, described in detail elsewhere.<sup>[19]</sup> Then, the conductivity of the materials was measured by running a heating scan from 15 °C at 1 °C h<sup>-1</sup>.

The electrochemical stability window of one-pot PYR<sub>13</sub>TFSI was evaluated by using it as an electrolyte component in LiTFSI/PYR<sub>13</sub>TFSI mixtures (1:9 molar ratio).<sup>[27]</sup> Vacuum-dried, carbon-rich (Super C45, IMERY) electrodes (ca. 1.13 cm<sup>2</sup>) were used as working electrodes with sodium carboxymethylcellulose (NaCMC, Dow Wolff Cellulosics, Walocel CRT 2000 PPA 12 with a degree of substitution of 1.2) as the binder (Super C45/NaCMC, 4/1 w/w). Lithium metal was used as counter electrode and a glass-fibre separator (Whatman GF/A) as separator. The LiTFSI/PYR<sub>13</sub>TFSI electrolyte samples were loaded into the Li/C cells (manufactured in a dry room), which were housed in soft envelopes and then vacuum-sealed. The Li/C cells were subjected to CV tests, performed at 0.5 mVs<sup>-1</sup> and 20 °C, by using a VMP3 (Bio-Logic SAS) potentiostat/galvanostat. Anodic CV was performed by scanning the cell voltage from the open-circuit voltage (OCV) up to 5 V versus Li<sup>+</sup>/Li<sup>0</sup> and then in the range of 3–5 V (vs. Li<sup>+</sup>/Li<sup>0</sup>). Cathodic CV was performed by initially scanning the cell voltage from the OCV down to 0.01 V (vs. Li<sup>+</sup>/Li<sup>0</sup>) and then cycling in the 0.01–1.00 V (vs. Li<sup>+</sup>/Li<sup>0</sup>) range. Separate cells, based on fresh samples each time, were manufactured for carrying out the voltammetry tests.

The electrochemical performance of the one-pot IL was also preliminarily validated by carrying out galvanostatic cycling tests on Li/Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> (Li/LTO) anode and Li/LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> (Li/NMC) cathode half-cells. The electrodes, prepared as reported elsewhere,<sup>[27]</sup> were composed of: 1) Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> (active material, 88 wt%, NANO-MYTE), Super C45 carbon (electronic conductor, 7 wt%, IMERY), and NaCMC (binder, 5 wt%) for the anode, whereby formic acid (1 wt% vs. Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>) was added to the slurry to give neutral pH; 2) LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> (92 wt%), Super C65 carbon (4 wt%, IMERY), and polyvinylidene difluoride (binder, 4 wt%, Solvay) for the cathode. The cells were manufactured in a dry room) by stacking an LTO or an NMC electrode (cast onto a 20 µm Al foil), a glass-fibre separator (Whatman GF/A) embedded in the LiTFSI-PYR<sub>13</sub>TFSI electrolyte and a lithium-metal electrode (500 µm, Honjo metal Co.). Then, the stack was housed in a vacuum-sealed, soft-pouch envelope. Al and Cu foils were used as the cathodic and anodic current collector, respectively. The cycling tests, run at 0.1C and 20 °C, were performed with a Maccor 4000 battery cyler.

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## Conflict of interest

The authors declare no conflict of interest.

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